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STRUCTURAL SPECIFICS OF POWDERED NITRIDE-CONTAINING MATERIALS (ALUMINUM AND BORON COMBUSTION PRODUCTS)

A. P. Il'in,[1] V. I. Vereshchagin,[1] A. A. Gromov,[1] and G. V. Yablunovskii[1]

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The results of studying the combustion products of aerogel mixtures of aluminum and boron ultrafine powders in air are discussed.

One of the problems emerging in the production of articles made of high-melting and heterogeneous components consists in the formation of transitory layers between the powdered components [1]. It was earlier shown that a mixture of ultradisperse aluminum powder and ASD-1 industrial aluminum powder on combustion in air produces powdered products containing approximately 50% AlN (here and elsewhere weight content is indicated) [2]. As a result of studying the microstructure using the electron microscope, it was found that the combustion products are spheroidal sinters 20 to 200 μm in diameter joined in easily broken associates of millimeter size. Of special interest are combustion products represented by needle-shaped formations although the initial powder particles were spherical. It was assumed that the observed modification of the particle shape was associated with mass-transfer processes during combustion [2]. The need for a thorough investigation of the structure and properties of these materials is related to the search for possible areas of application for nitride-containing combustion products.

The present paper describes the results of studying the products of combustion of aerogel mixtures of aluminum and boron ultrafine powders (UFP) in air. It was previously shown that a boron UFP additive (9%) introduced to the aluminum UFP does not decrease the content of bound nitrogen, which is 13.3% and 13.5%, respectively, for the aluminum UFP and the aluminum and boron UFP [3], but the study was not detailed enough. The assignment of the considered objects to aerogels is related to the low bulk density of the UFP, which is 0.1 – 0.2 g/cm^3 [4]. The content of metallic aluminum in the UFP was 90.8%, and the specific surface area was 6.5 m^2/g. The aluminum UFP was obtained by electric explosion of the conductors in gaseous argon [5].

The boron UFP used in the study was obtained by the calcium-thermal method and had a specific surface area of 11 m^2/g. The boron particles were agglomerates which easily break under mechanical action. The elemental boron content in the UFP was 94%. The aluminum and boron UFP mixtures were prepared by mechanical dry mixing and multiple sifting on a sieve with a cell size of 63 μm. The mixtures were poured on a stainless steel base and a truncated conical shape was imparted to the sample. The combustion process was initiated with a nichrome spiral.

The combustion of the mixtures of aluminum UFP with boron UFP additives up to 30% was studied for a fixed sample weight equal to 4 g. The temperature was measured by a VR 5/20 thermocouple whose junction was protected by a ceramic cap; therefore the obtained values were not absolute. With increase in the boron content of the boron and aluminum UFP mixture, the maximum temperature first increases and then decreases, its maximum corresponding to a boron content of 15 – 20%. The overall combustion duration, i.e., the time between the ignition and the moment the samples attain the temperature of 660 C in cooling, varies linearly with increase in the boron content.

According to the x-ray phase analysis (DRON-3M diffractometer, MoK_α-radiation), the dependence of the content of AlN in the combustion products on the amount of boron in the initial mixture follows the maximum temperature dependence, i.e., it passes its maximum with the boron content equal to 20%. An increase in the AlN content occurs simultaneously with a decrease in the quantity of residual Al^0 and α-Al_2O_3 in the ultimate combustion products. It should be noted that the x-ray phase analysis did not identify boron nitride and boron oxide among the combustion products.

[1] High-Voltage Science and Research Institute at Tomsk Polytechnical University, Tomsk, Russia.

The content of bound nitrogen was determined by chemical analysis using the Kjeldahl method. The measurement error was ±0.4%.

Boron UFP content in the initial mixture containing aluminum UFP, %	Nitrogen content in the combustion products (according to Kjeldahl), %
0	9.8
5	12.3
9	13.2
15	13.8
20	14.2
25	14.0
30	11.1

It can be seen that with an increase in the boron content of the initial mixture up to 20%, the amount of bound nitrogen increases from 9.8 to 14.3%, but with a 30% boron content in the mixture, the amount of nitrogen decreases to 11.1%.

The combustion specifics of the samples with different weights (0.5 – 15.0 g) were studied on a mixture of aluminum UFP with 15% boron. As the sample weight increases to 4.0 g, the maximum combustion temperature rapidly grows, and for larger sample weights (starting with 8.0 g), the temperature increase is slowed. The combustion of samples weighing less than 0.5 g proceeds in a single stage with trace quantities of bound nitrogen in the composition of the resulting products.

According to the x-ray phase data (the relative intensities of 100% reflections on the x-ray patterns of the combustion products), as the sample weight increases, the content of AlN ($d_{100\%}$ = 2.695 Å) increases and the content of the residual aluminum ($d_{100\%}$ = 2.34 Å) and α-Al_2O_3 ($d_{100\%}$ = 2.085 Å) decreases. The dependence of the AlN content is similar to the dependence of the temperature on the sample weight, and for the residual aluminum and α-Al_2O_3 a reverse dependence is observed. The x-ray phase analysis data correlate with the results of the chemical analysis which determined the bound nitrogen content in the ultimate combustion products of samples with different weights:

Weight of the initial sample of UFP mixture (Al + 15% B), g	Nitrogen content in combustion products, %
0.5	9.8
1.0	12.1
2.0	12.9
4.0	14.1
8.0	14.5
15.0	15.3

The highest content of bound nitrogen (15.3%) corresponds to the largest sample (15 g) of the initial mixture. It should be noted that the bound nitrogen content as a function

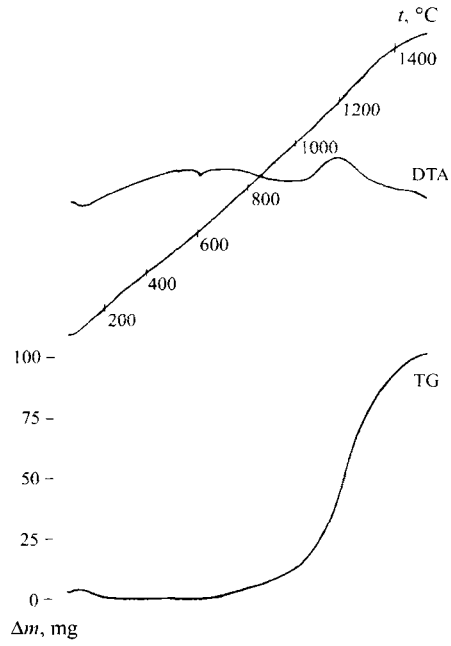

Fig. 1. Derivatogram of the combustion products of aluminum UFP mixed with 10% boron (m = 288 mg, heating rate 15°C/min in air; reference standard α-Al_2O_3).

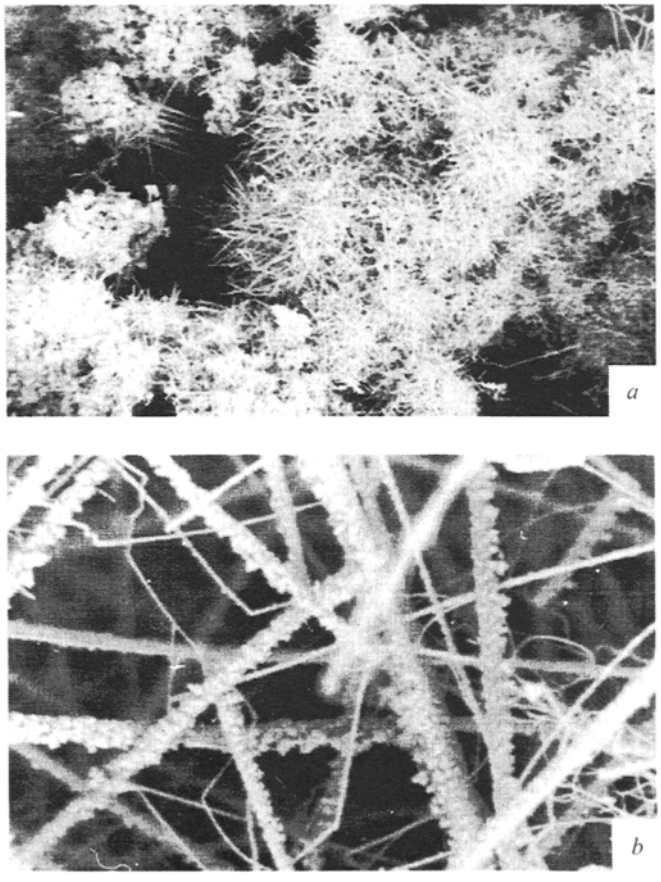

Fig. 2. Electron microscope photos of the combustion products of aluminum UFP mixed with 10% boron at magnification of ×1000 (*a*) and ×3000 (*b*).

of the sample weight does not attain the maximum in the terms of the performed experiment.

The products of aluminum UFP combustion in air are formed at high temperatures reaching 2200 – 2400°C (a LOP-72 pyrometer) [6]. In this case the combustion of aluminum nitride is not completed, which is probably associated with its encapsulation in the products with a higher oxidation resistance. As the ultimate combustion products of the mixture of aluminum UFP with 20% boron are linearly heated (Q-1500 derivatograph) up to 1500°C, an increase in the sample weight is observed in the temperature range above 660°C, which is seen in the TG curve (Fig. 1).

According to the DTA, an endothermic effect caused by the fusion of the residual aluminum is registered at the temperature 660°C, and an exothermic effect is recorded at 1070°C, which is accompanied by an increase in the rate of weight growth of the heated sample. The temperature at which intense weight growth starts was found according by the Piloyan method [7] to be 660°C, and it corresponds to the aluminum melting point. The aluminum compounds identified in the composition of the aluminum UFP ultimate combustion products do not have noticeable volatility within the considered temperature range (no decrease in weight is observed) and the oxidation of aluminum and aluminum nitride in oxygen is accompanied by an increase in weight.

Figure 2 shows the photos of the ultimate products of the combustion of aluminum UFP mixed with boron in air. Whereas the initial powders are agglomerates of spheroidal particles significantly less than 1 μm in diameter [5], the combustion products form a skeleton spongy structure (Fig. 2*a*). The structural fragments comprising the skeleton are needle-shaped crystals several tens of micrometers long and 1 – 10 μm thick, which consist of smaller fragments whose typical size is below 1 μm. Thus, taking into account the microstructural characteristics of the ultimate combustion products of aluminum UFP in a mixture with boron UFP (the needle-like shape of the crystals), it can be assumed that the process of their formation proceeded with participation of intermediate gaseous products, especially since the needle-shaped crystals are produced by evaporation and condensation methods [8].

The mechanism of nitride formation in the combustion of ultrafine powders is complicated: the formation of the ultimate products is affected by specific thermophysical and kinetic properties as well as by the thermodynamic state [9]. The effect of the thermophysical processes on the combustion is probably determined by the existence of the "critical weight" of the UFP sample: when the weight is below critical, the combustion process proceeds in a single stage with trace quantities of bound nitrogen in the ultimate products, and when the weight is above "critical," it proceeds in two stages with a substantial amount of nitride. The existence of a luminescent area above the burning powdered metals and boron is related to the presence of the initial compounds or their oxidation products in the gaseous state [10]. The participation of the gaseous phase in the formation of the ultimate products determines their microstructure, i.e., the needle-like shape of the polycrystals [10, 11]. According to the DTA data, the end products are oxidation-resistant, which suggests the encapsulation of the aluminum nitride and residual aluminum phases in the oxide phases.

Thus, the substructural characteristics (a complex arrangement of different phases in the particles) of the powders makes them promising for the production of composite materials. The formation of nitrides significantly decreases the UFP combustion heat, since aluminum oxidation to the nitride yields 2.5 times less heat than its oxidation to the oxide [12]. It should be noted that the experimentally determined regularities are probably true only for aerogel ultrafine powders.

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